C S P The DOE Center of Excellence for the Synthesis and Processing of Advanced Materials

Basic Energy Sciences
Division of Materials
Sciences and Engineering

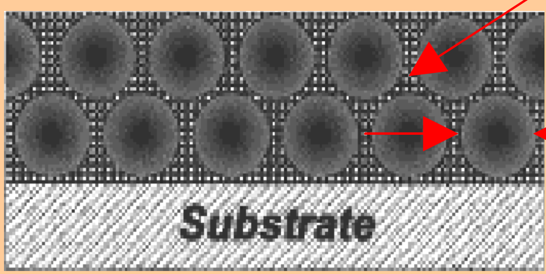
Smart Structures Based on Electroactive Polymers

Greg Exarhos, Coordinator, PNNL

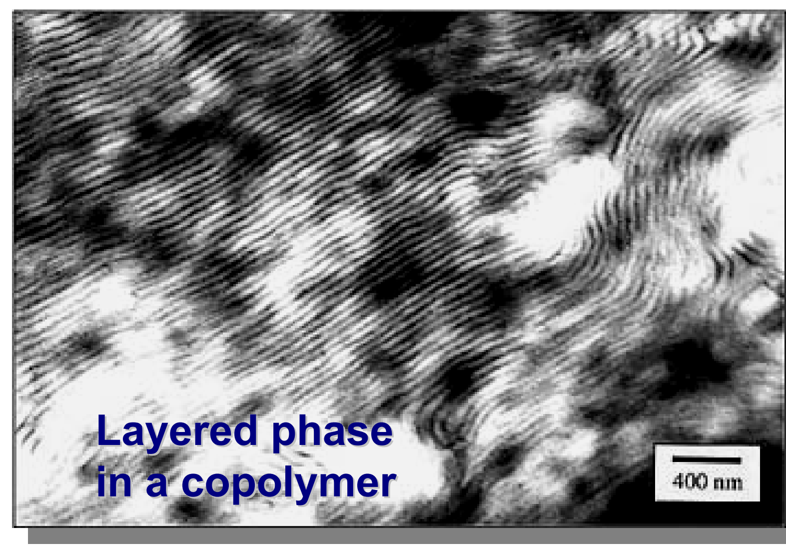
Design and synthesize functionalized molecules that self-assemble into predicted hierarchical architectures and that show a predetermined and reversible response to applied stress

Templated Nanostructure

25-100 nm Au particles



1 µm “pores”



>>> Topical Areas Addressed <<<

Polymer Synthesis / Processing

Self-Assembly and Templating

Modeling Polymer Interactions

Chemical Surface Modification

Directed Phase Transformations

Structure/Property Relationships

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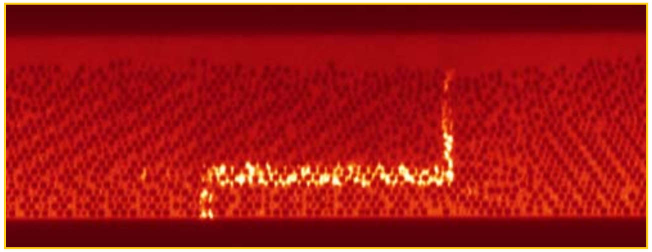
Motivation

Polymer waveguide (yellow) embedded in a 3D photonic crystal (black dots).



- **Challenge:** Understand how molecular organization and evolution of hierarchical structures is controlled by resident chemistry (bottoms-up processing) and how the attendant structure influences materials response
- **Focus:** Identify phenomena that can be exploited to impart "smartness" to a material
  - Reversible structural transformation (eg. order <--> disorder)
  - Physical property dependence on external variable
    - Refractive index (temperature, light intensity, pressure, pH,…)
    - Volume change (pH, solvent ionicity, temperature, electric field,…)
    - Surface hydrophobicity or hydrophilicity (solvent polarity, pH,…)
  - Structure/property relationships (theory/experiment integration)
- **Outcome:** A framework for the rational design of materials with molecularly-engineered structures that are self-regulating
  - Ion-selective membranes (controlled sequestering and release)
  - Color-shifting material (camouflage, architectural, optical limiting)
  - Controlled release (proteins, drugs, water,…)

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Research Distributed Among Three Tasks

- **Molecular Self-Assembly in Polymer Systems**
  - Co-Polymer synthesis and functionalization
  - Self-assembly approaches to generate specific architectures
  - Development of hierarchical porosity
  - Magnetic resonance characterization
  - Structural dependence on solvent polarity
  - Modeling polymer chain interactions

Los Alamos NATIONAL LABORATORY

ARGONNE

Ames Laboratory

Pacific Northwest National Laboratory

OAK RIDGE NATIONAL LABORATORY

- **Induced phase transformations in co-polymer systems**
  - Volumetric response to applied stress
    - Temperature
    - Electric Field
  - Polymer-metal nanocomposites

ILLINOIS UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

BERKELEY LAB

Pacific Northwest National Laboratory

- **Synthesis of oriented polymer nanowires**

Pacific Northwest National Laboratory

INEEL

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Molecular Self-Assembly in Polymer Systems

Ames, ANL, LANL, LLNL, ORNL, PNNL

Innovative synthesis and processing methods generate tailored molecular architectures that influence properties.

- **Driver** - **Self-assembly and structural evolution in polymer melts or solutions are controlled by both inter-and intra-molecular interactions among the resident hydrophilic and hydrophobic regions, their respective number density, and size.**
- **Key research issues**
  - **What factors control hierarchical structural development, dimensions of constituent phases, pore size and distribution?**
  - **How are resulting structures characterized at the nanoscale?**
  - **What chemical (physical) factors lead to structural modification?**
- **Future directions**
  - **“Computational molecular synthesis”**
  - **How is chemical functionality integrated?**
  - **How can self-organization be achieved in nominally inorganic polymer systems?**
  - **What factors control the crystalline nature of the resident phases and phase boundaries?**

Brush-graft copolymer through a living polymerization process (ATRP)

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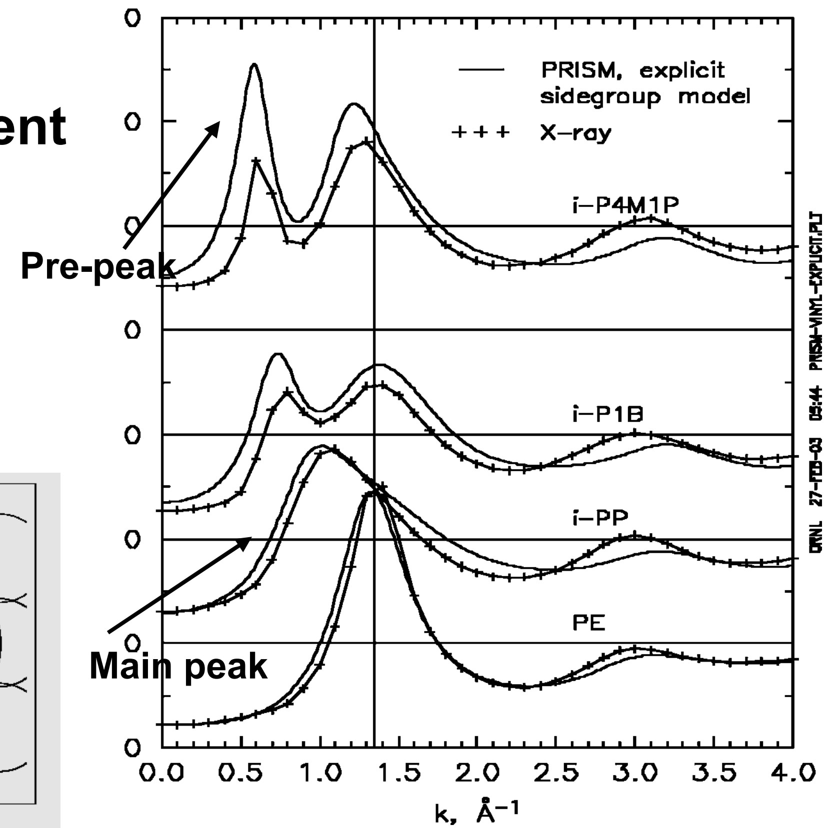
Virtual Center for Synthesis & Processing

A. Habenschuss, M.-H. Kim (ORNL), J.G. Curro, D. R. Heine (SNL)

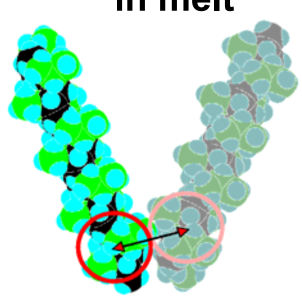
- **Model localized polymer site interactions to understand how chemistry influences structure (PRISM code)**
- **The “Pre-peak” in vinyl polymer melt X-ray structure factors correlates with helix-helix packing distance in corresponding crystals**
- **Realistic, explicit side-group PRISM model calculations in good agreement with experiment**
- **Implies helical regions in melt**



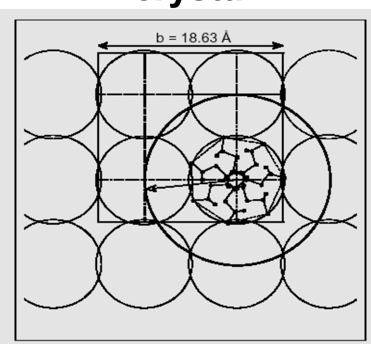
X-ray, PRISM

Main peak: Chain-chain correlations in melt	Pre-peak: Helix-helix correlations in melt	Helix-helix distance in crystal

PE



P4M1P



Crystal structure of i-P4M1P.

P4M1P

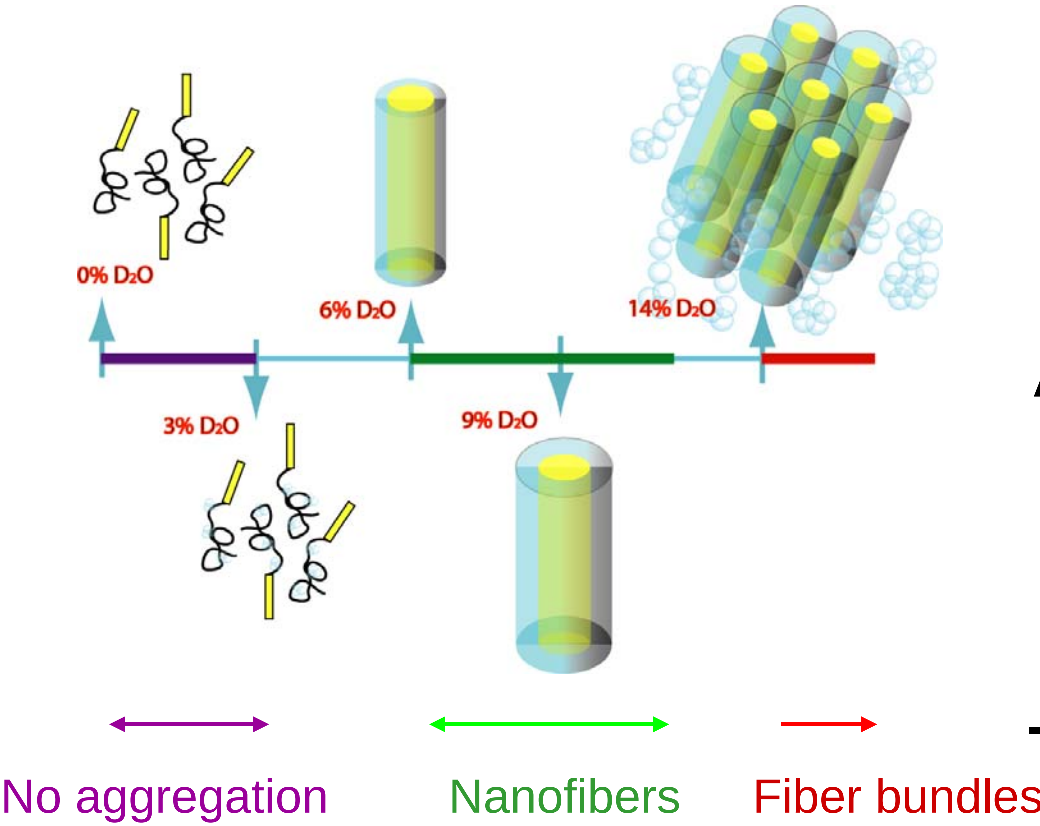
Technical Results

- The melt structures of linear polyethylene and the isotactic vinyl polymers - polypropylene, poly(1-butene) and poly(4-methyl-1-pentene) - with the corresponding methyl, ethyl and isobutyl side chains, were recently studied with wide-angle X-ray diffraction.
- As the size of the side-branch increases from zero (PE) to methyl, ethyl and isobutyl, a “pre-peak” appears below the main diffraction peak in the carbon-carbon structure factor.
- This pre-peak shifts to lower scattering vectors with increasing bulkiness of the side group.
- Earlier Polymer Reference Interaction Site Model (PRISM) calculations based on a simple model of the vinyl chains, where the side group is represented as a single scattering site with different site diameters, qualitatively captured the pre-peaks seen in experiment.
- New PRISM calculations were completed using a realistic model of vinyl polymer chains and compared with the results of the X-ray studies and the earlier PRISM calculations.
- This result furthers our understanding of the structure and packing in non-crystalline polymer materials; relevant to compatibility of polymer blends.

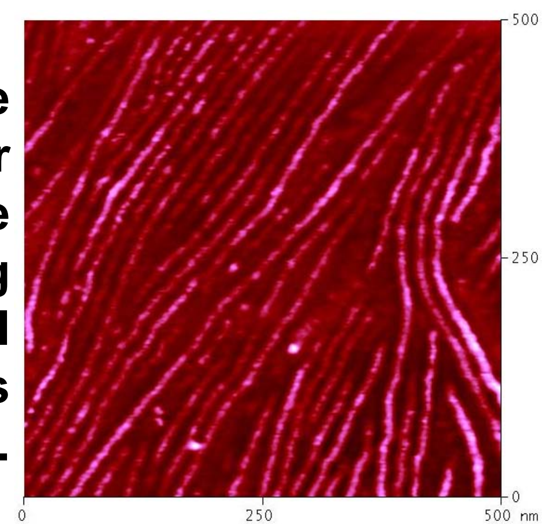
Structural Ordering of Block Co-Polymers in Solution

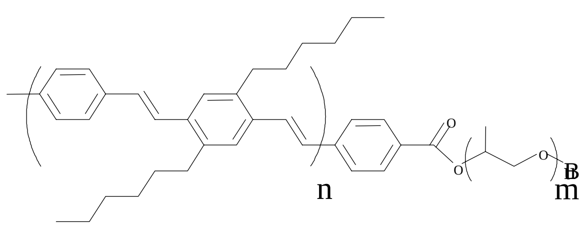
H. Wang, ANL

- Fiber diameter and length in OPV-PEG is controlled by block lengths
- Substitution of the more hydrophobic PPG for PEG perturbed phase stability causing fibers to bundle at high water additions



AFM image of a fiber bundle showing individual nanofibers - 18 nm dia.

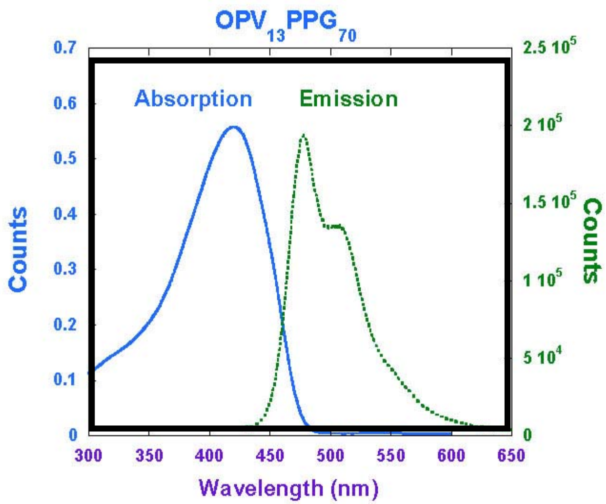


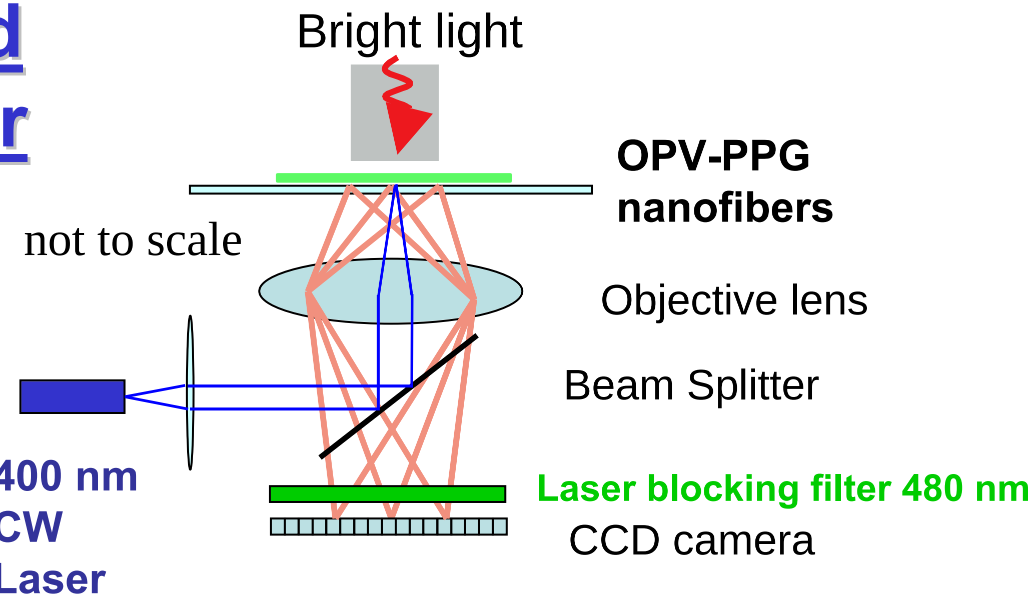


OPV_n - PPG_m

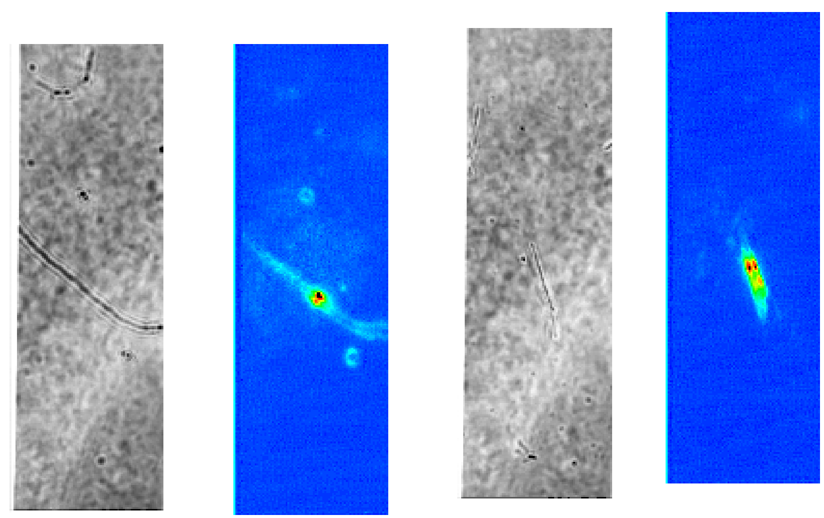
Photoluminescent and wave guiding behavior

Absorption and emission spectra of OPV_{13}-PPG_{70} in THF





Bright light image



Fluorescence images

- Gray scale bright light images of two OPV_{13}-PPG_{70} fiber bundles (Image size: 32×102 mm)
- Each fiber bundle was locally excited at 400 nm and detected at 480 nm showing fluorescence from the entire fiber bundle.

Reversible Hierarchically Assembled Block Copolymers in Solution

S. Mallapragada, Ames, T. Thiyagarajan, ANL

Synthesize pentablock copolymers of PDEAEM, PEO, and PPO via atom transfer radical polymerization (ATRP) and characterize phase stability as a function of pH.

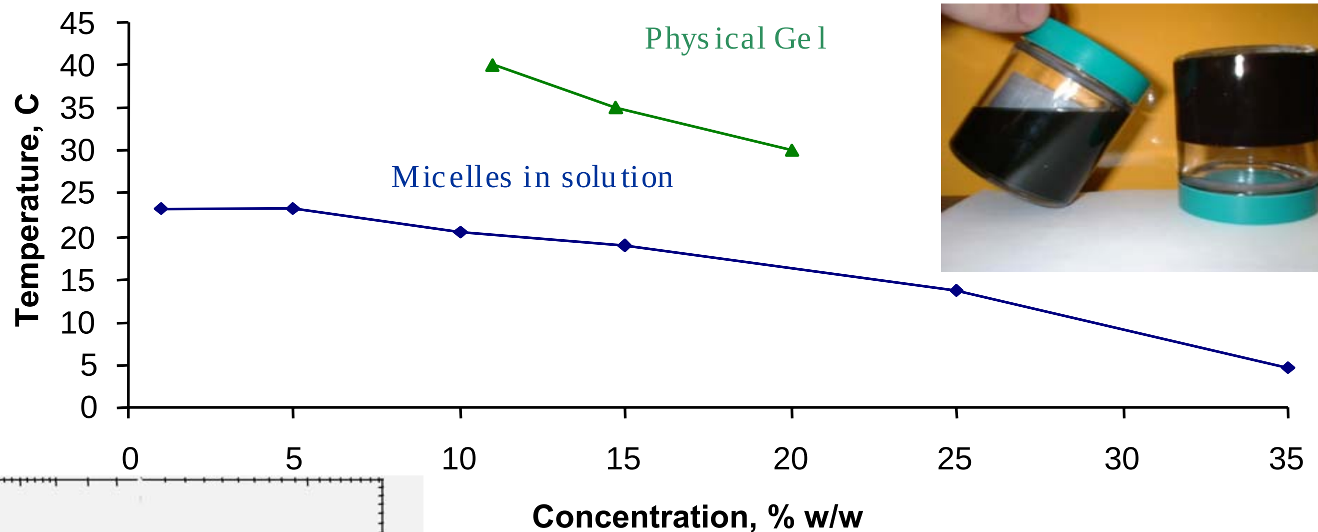
Cryo-TEM image of polymer micelle

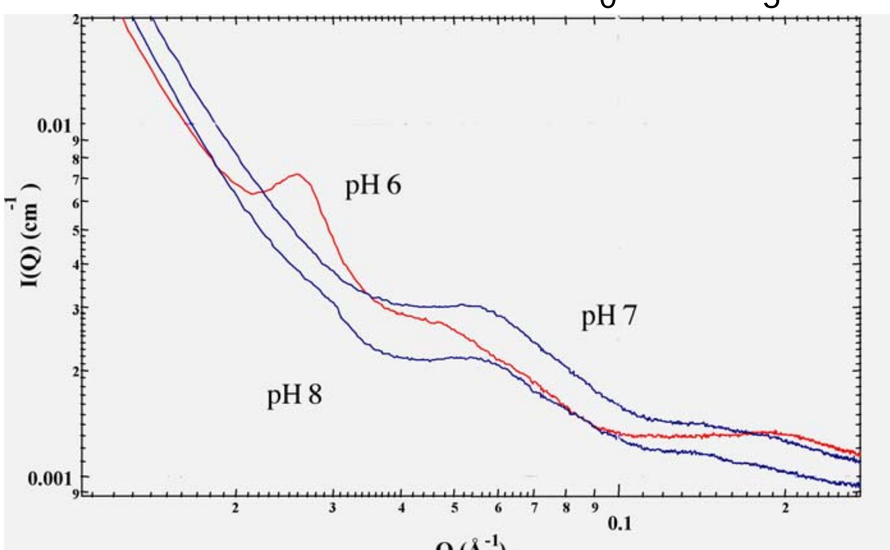
Self-assembly of micelles into a macroscale solid

- First observation of reversible self-assembly of block co-polymer micelles in solution to form a gelled solid with an elastic modulus similar to rubber
- Low pH solubilizes gel due to electrostatic repulsions between charged cations on the polymer chains
- At high pH, the consolidated gel is relatively insoluble

Phase Transitions of Petablock Co-Polymers at pH 7

Reversible self assembly in aqueous solution forms micelles that entangle above a critical gelation temperature and pH to form physical gels and macromolecular solids.





pH dependence of the scattering vector of a 25 w/w% petablock copolymer in solution.

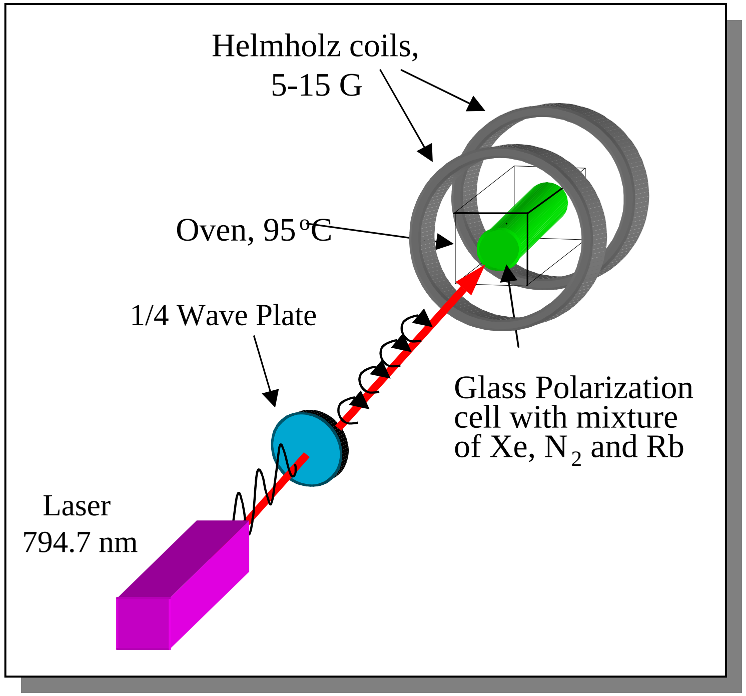
Since PDEAEM is hydrophilic at low pH and hydrophobic at high pH, the micelle structure can change considerably with pH as suggested by small angle X-ray scattering measurements

HP ^{129}Xe NMR Characterization of Porosity

PNNL, LLNL, LANL, NRC (Canada)

Pore structure and connectivity in nanoporous architectures is probed by means of magnetic resonance spectroscopy that uses spin polarized xenon atoms to interrogate local chemical environments during percolation through the structure.

Enhanced magnetic resonance signals are produced by optically pumped xenon atoms as they diffuse through the the material of interest.

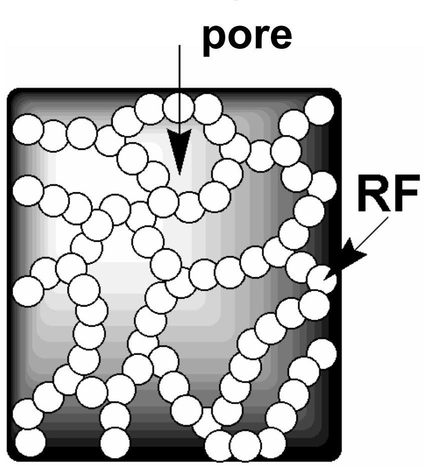


Synthesize resorcinol-formaldehyde (RF) polymers. Vary R, F and amount of catalyst to study how composition is related to resident porosity.

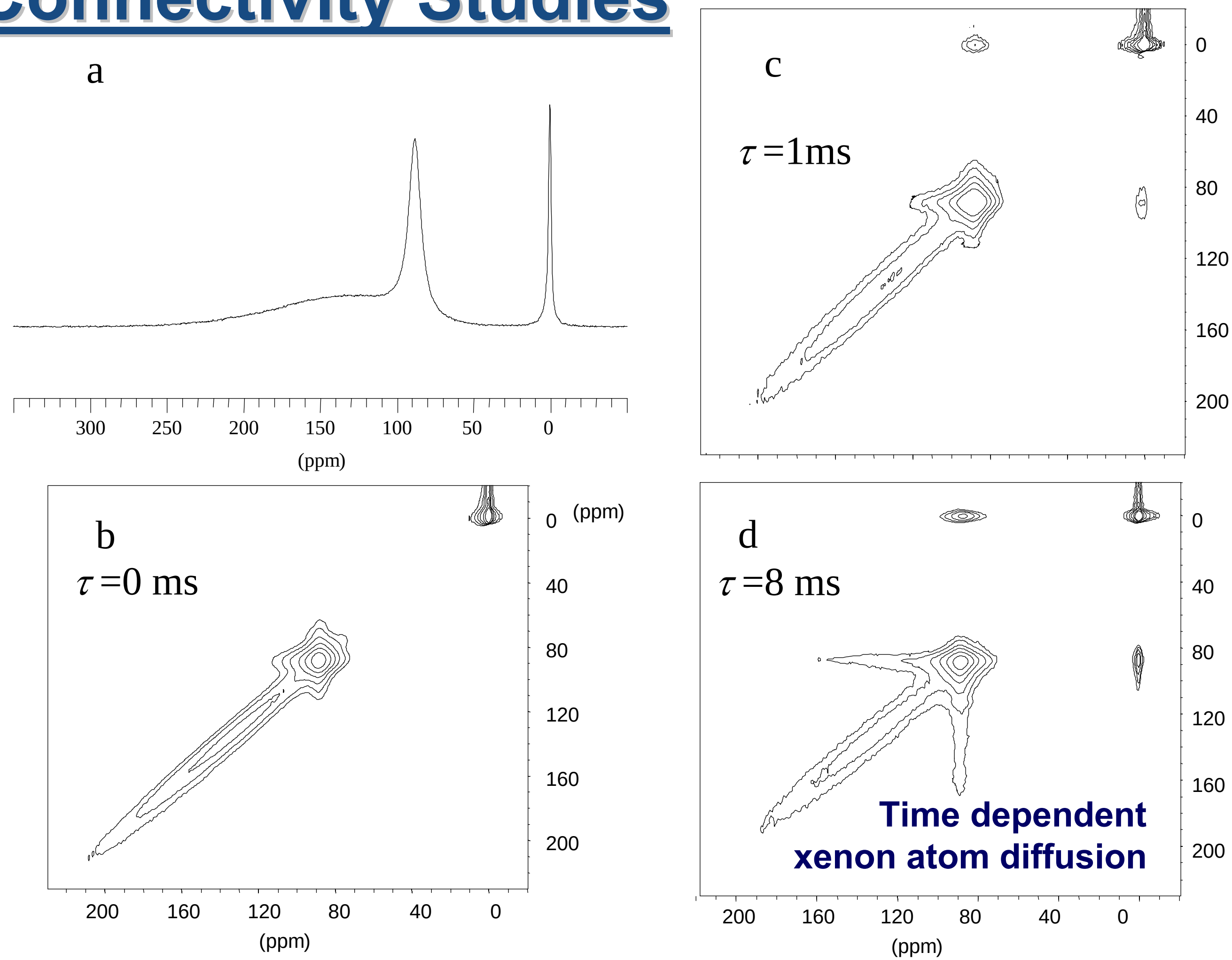
The pore structure and interconnectivity in aerogels are determined at the nanoscale from time dependent magnetic resonance studies.

NMR results are to be correlated with neutron scattering studies.

Molecular picture of Polymer Aerogel

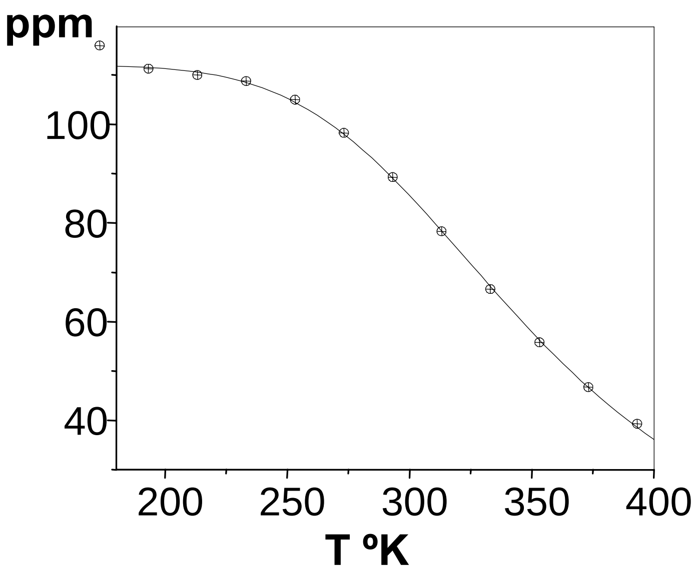


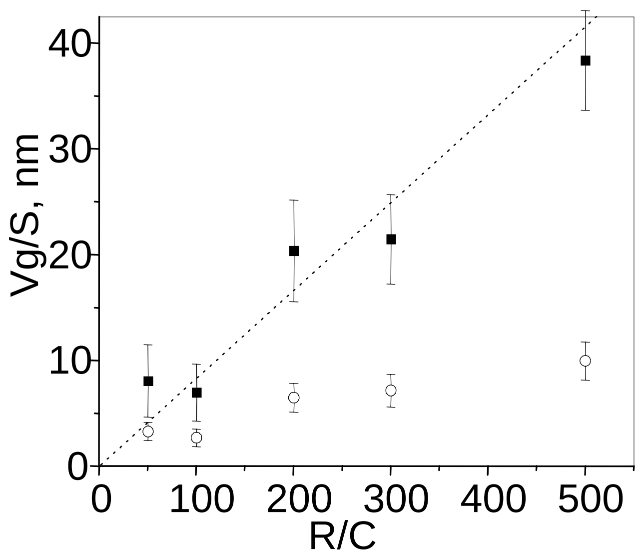
Pore Connectivity Studies



(a) CF HP 129Xe NMR spectra for RF aerogels prepared with an R/C ratio of 300. (b)-(d) CF HP 2D EXSY 129Xe NMR spectra for RF aerogels (R/C=300) recorded with t as indicated. All spectra were obtained at 293 K with a HP Xe flow rate of 45 sccm.

Magnetic Resonance Data Identify Pore Sizes and Determine Surface Area

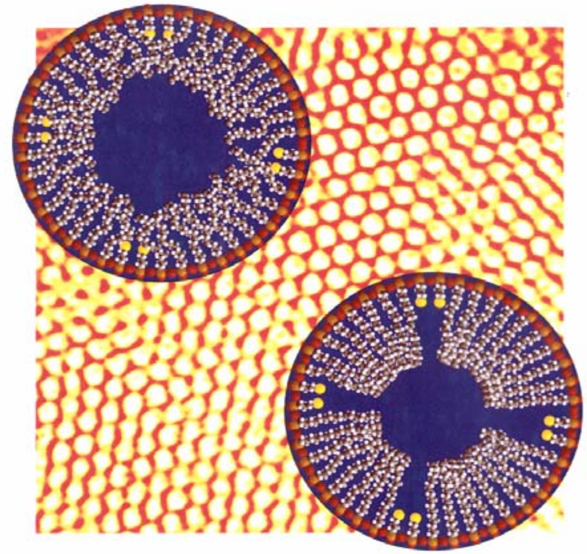




(A) The ^{129}Xe chemical shift plotted as a function of temperature for the narrow signal arising from the mesopores in RF aerogels (R/C=300). The solid dots are experimental data obtained from CF HP ^{129}Xe NMR spectra recorded at 20 K intervals, and the solid line is a theoretical fit. (B) The Volume to Surface-area ratio Vg/S as a function of R/C ratios from Xe NMR and N_2 adsorption data.

Induced Phase Transformations in Polymer Systems

UI/MRL, LBNL, PNNL, SNL



Invoke transformation phenomena in polymeric materials to achieve a reversible change in physical properties under the influence of an applied stress

- **Driver - Investigate the dependence of an applied external agent on structural ordering phenomena and resident surface chemistry (temperature, pH, oxidation state, ionicity, applied potential)**
- **Key research issues**
  - **How are structural changes related to an applied external stress?**
  - **How do structural changes control the adsorption and/or release of sequesterants?**
  - **What is the implication for molecular sensor sensitivity/specificity?**
- **Future directions**
  - **Design chemical functionality into polymers systems to impart multifunctionality.**
  - **Investigate robustness of stress induced phase transformations.**

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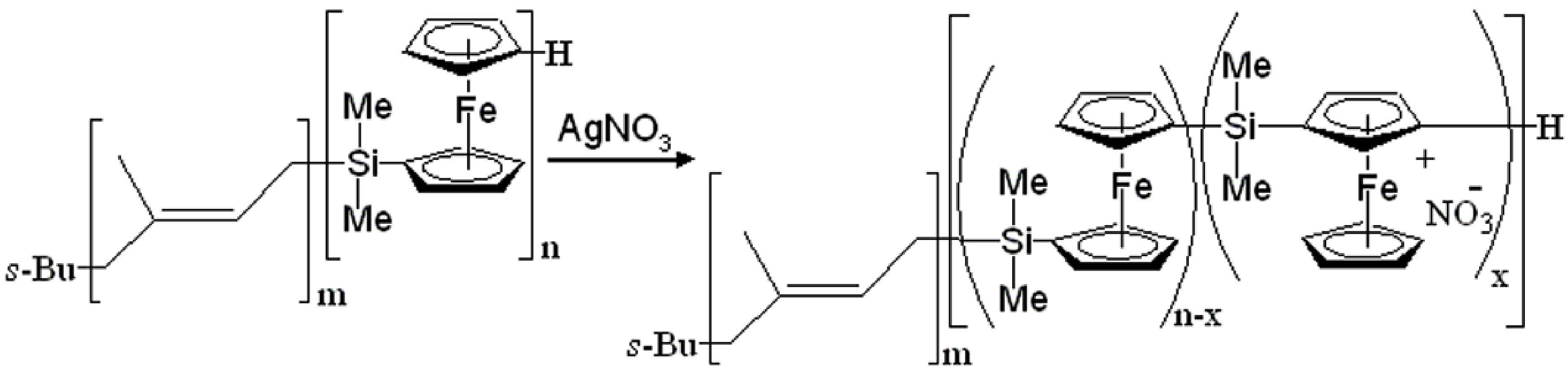
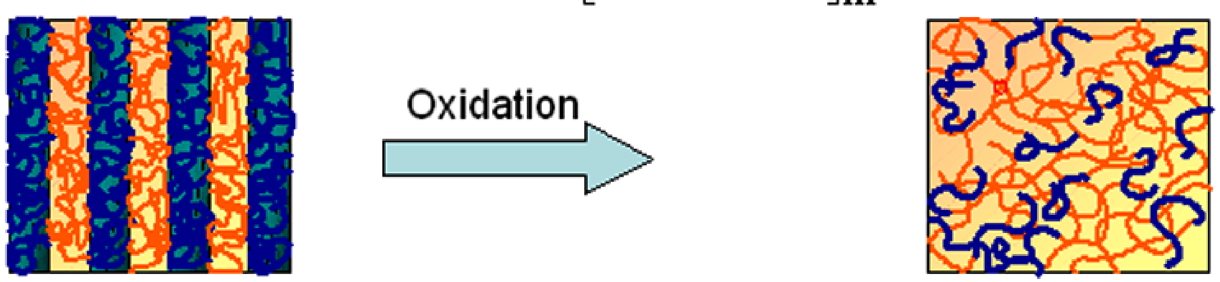
Effect of Chemical Oxidation on the Self-Assembly of Organometallic Block Copolymers

H.B. Eitouni and N.P. Balsara, LBNL

Control the spontaneous formation of ordered domains in soft materials by altering the oxidation state of attendant redox-active species.





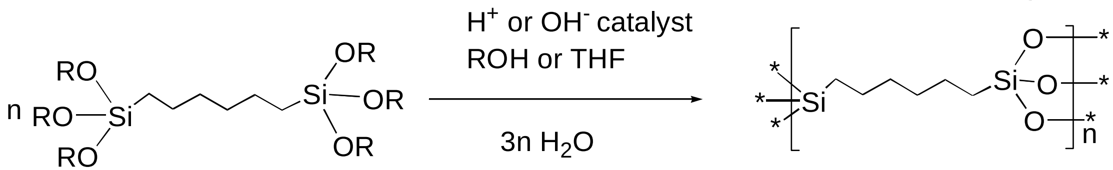
Ferrocene to ferrocinium cation transformation is driven by reaction with Ag^+

Application of small electric fields (2 V/cm) also effective for inducing the transformation.

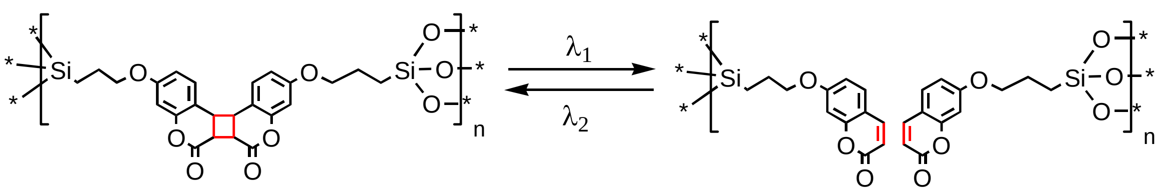
Fundamental Studies into Molecular & Nanoscale Origins of Structure and the Construction of "Smart" Sol-Gel Materials

D. A. Loy (PI), K. DeFriend, J. Stoddard, J. Small, K. Wilson, LANL

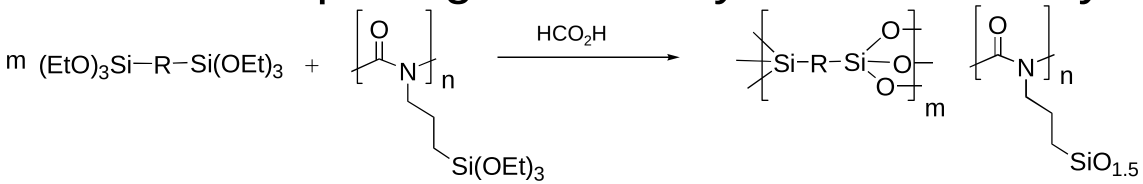
1) Passive Molecular Level Control of Porosity



2) Active Molecular Level Control of Porosity

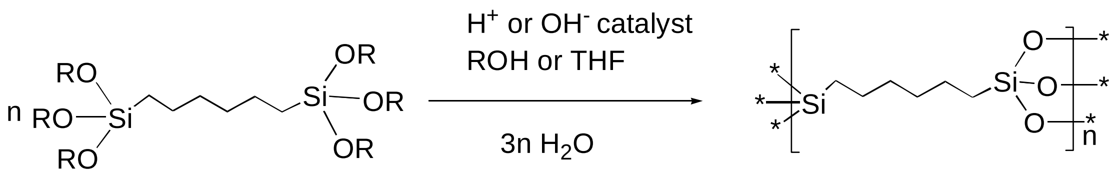


3) Nanoscale Templating of Porosity & Functionality



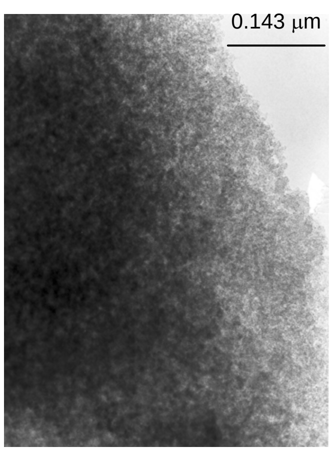
Passive Molecular Level Control of Porosity

Hyper-Crosslinked Hybrid Organic-Inorganic Materials



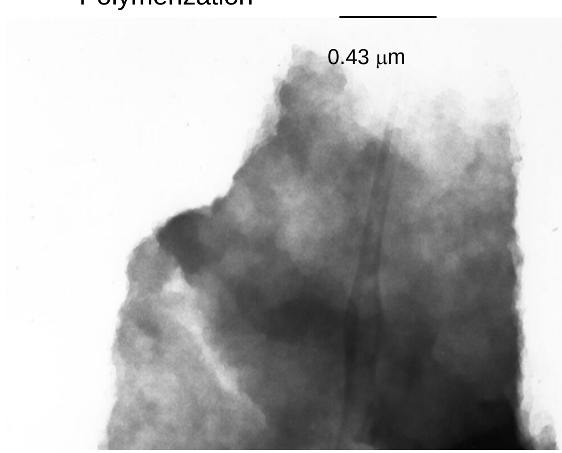
-Porous or Non-Porous on Command (catalyst or organic bridge)
-Network Compliance & Pore Collapse During Drying Controlled at Molecular Level

Base-Catalyzed Polymerization



Porous

Acid-Catalyzed Polymerization



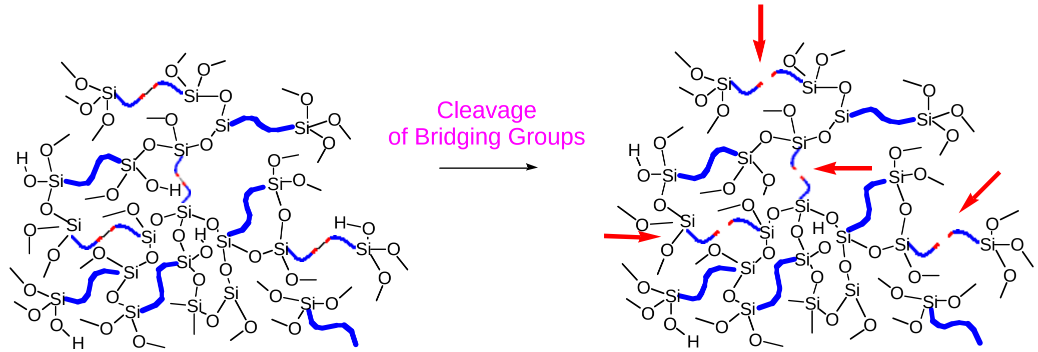
Non-Porous

Dense Separation Membranes for:
- *Hydrogen: Methane*
- *Carbon Dioxide-Methane*
- *Olefin-Paraffin*

K. DeFriend, J. Small, K. Wilson,LANL
Collaboration with:
K. J. Shea at UC Irvine
C. Cornelius at Sandia National Labs

Active Molecular Level Control of Porosity

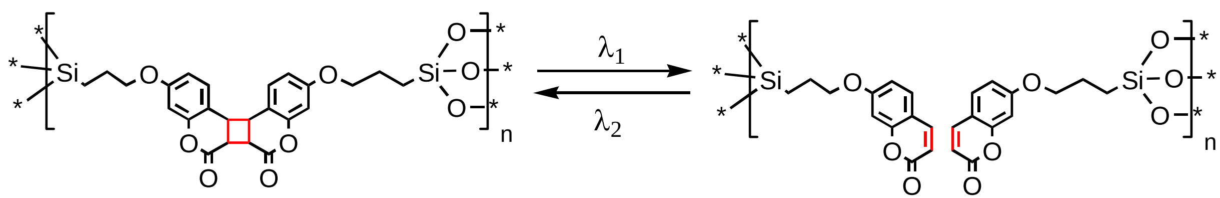
New Approach to Environmentally Responsive Sol-Gels & Membranes

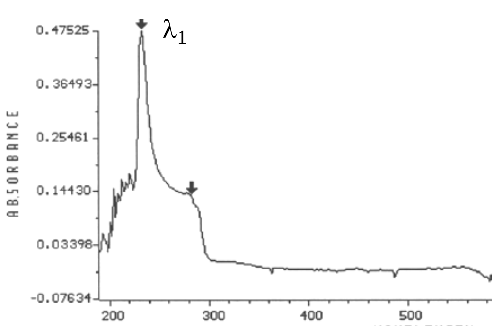


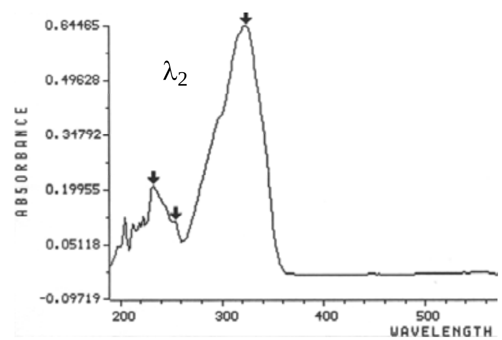
-Sol-Gel Hybrid Organic-Inorganic
-Coumarin Dimer Weak-Link

-Wavelength Specific Switch
-Reversible Transformation

-Variable Permeability
-Challenging Synthesis



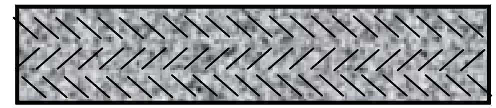




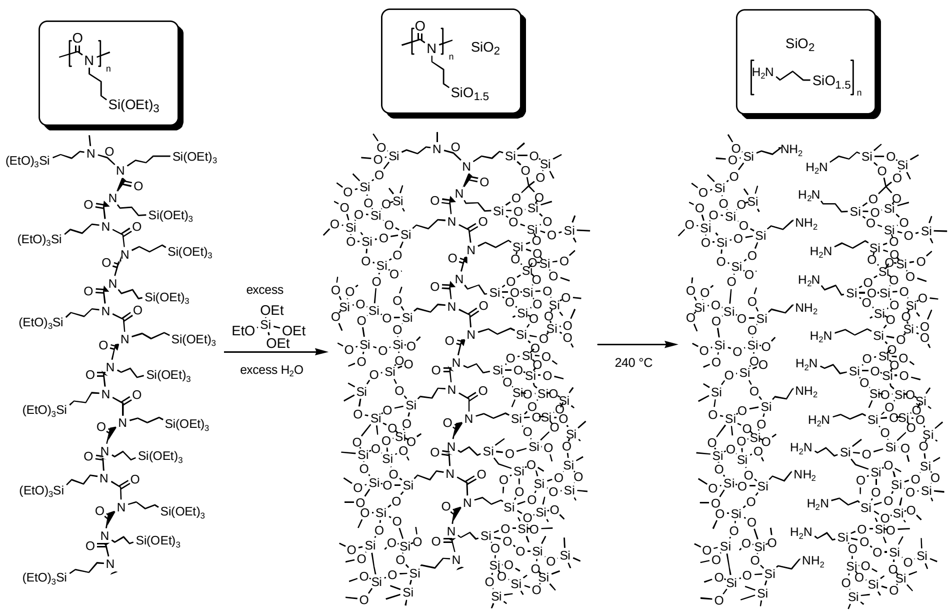
• Membranes • Tool for Structural Investigations •
• D. A. Loy, LANL
• Collaboration with Shea at UC Irvine & Cornelius at Sandia •

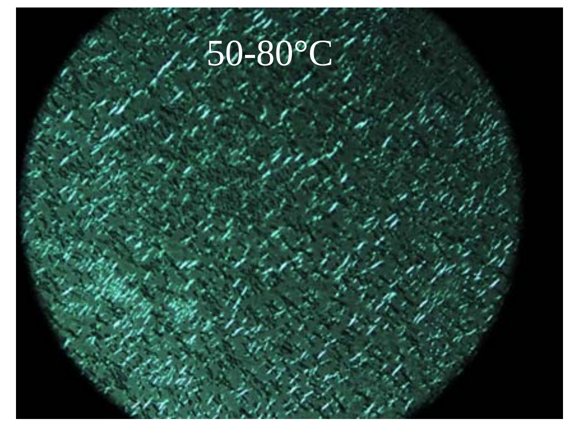
Nanoscale Templating of Porosity & Functionality

Hyper-Crosslinked Hybrid Organic-Inorganic Materials
Rigid Rod, Liquid Crystalline Nylon-1 Template
Functionalized Anisotropic Pores



Liquid Crystallinity organizes Templates





Nylon-1 Soluble in
Sol-Gel Monomers

• Gas & Fuel Cell Membranes • Facilitated Transport• Proton Transport Mechanisms •

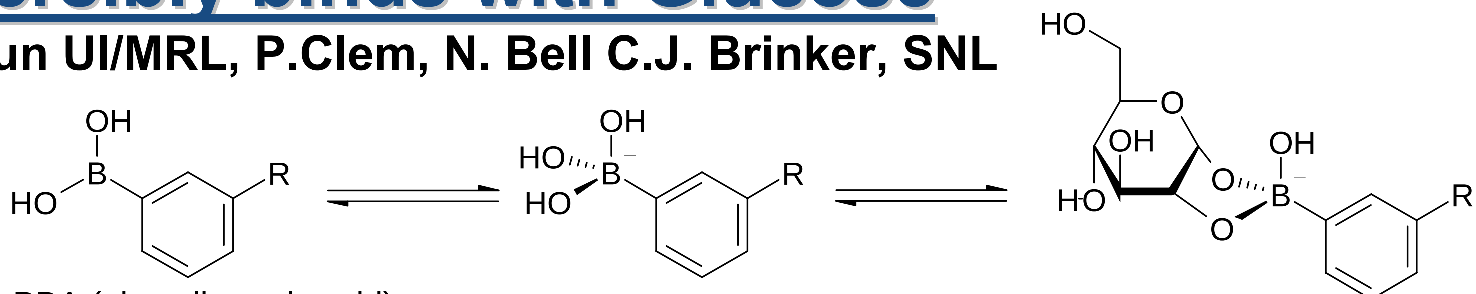
• *J. Stoddard, D. A. Loy, LANL*

NNSA

Los Alamos

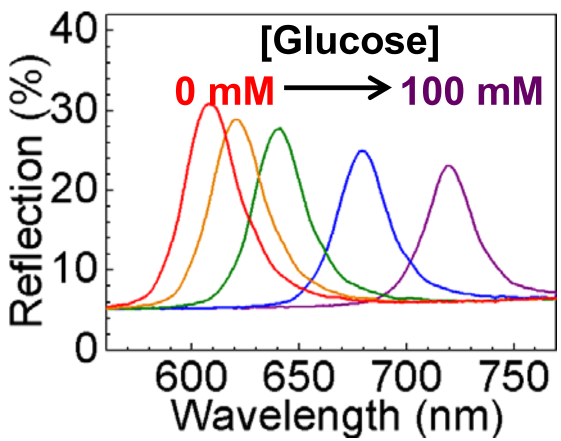
Sensor Based upon a Copolymer Hydrogel that Reversibly binds with Glucose

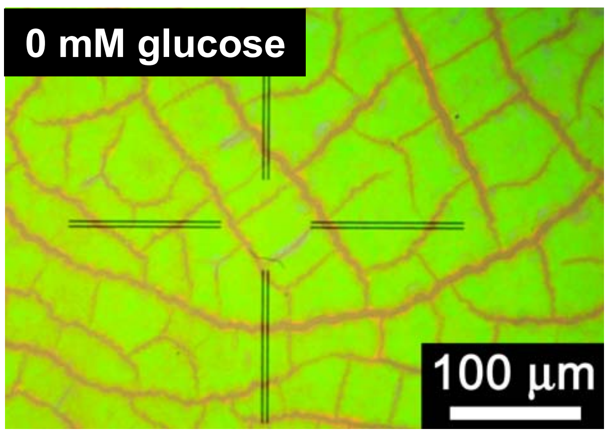
P. Braun UI/MRL, P.Clem, N. Bell C.J. Brinker, SNL

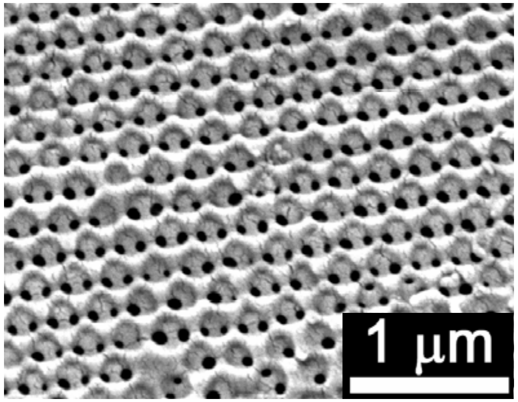


PBA (phenylboronic acid)

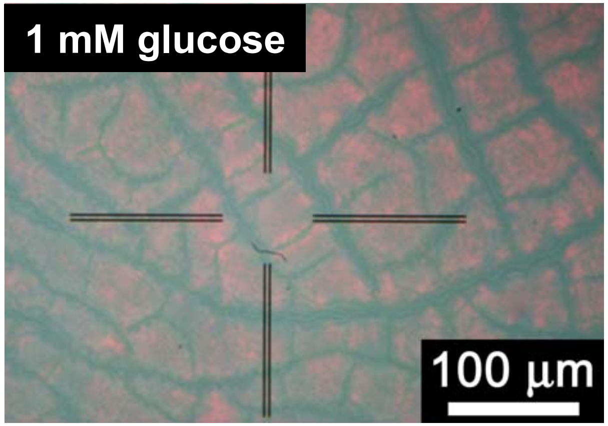
Glucose-PBA complex





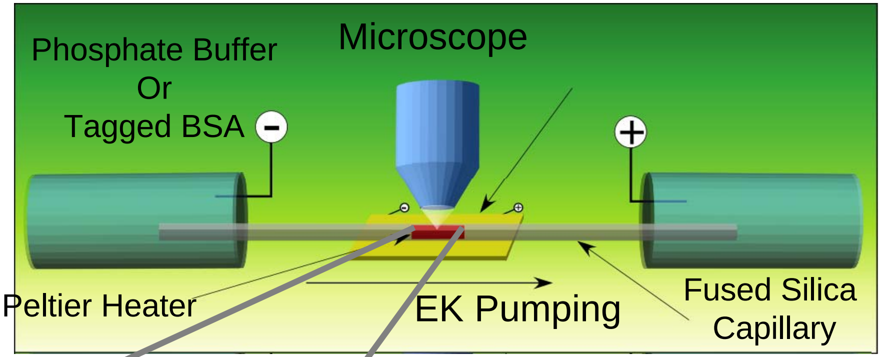


SEM of templated hydrogel

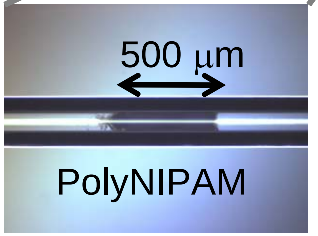


In-Situ Polymerization Process Yields High Surface Area Pre-Concentrator for Proteins

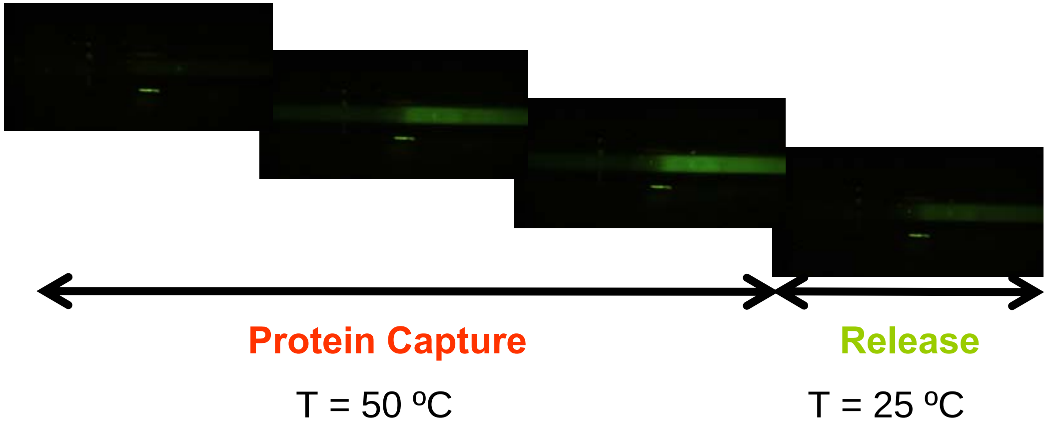
B. Bunker SNL, in collaboration with LANL and SMC, UT-Dallas



Protein adsorption experiments are conducted using electrokinetic pumping of dilute protein solutions through capillary columns.



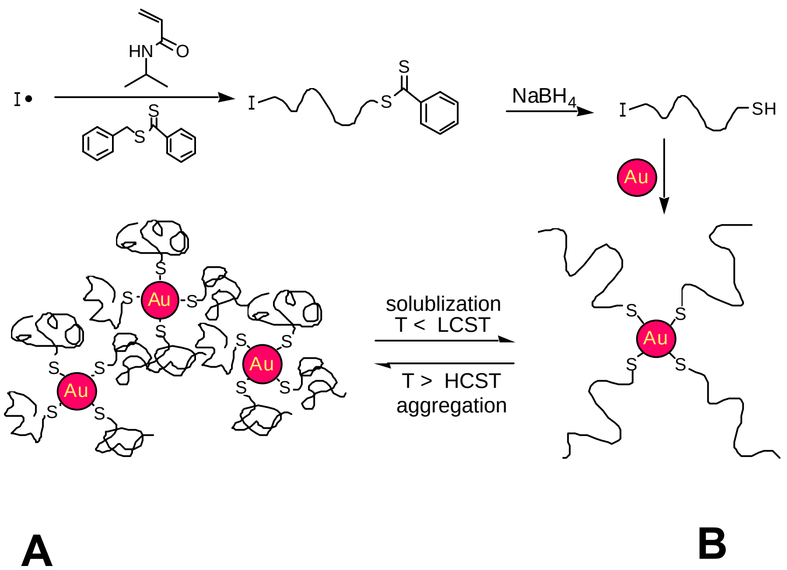
PNIPAM plug is polymerized in place.



PNIPAM-modified capillary column shows high efficiency for protein capture and exceptional (>95%) reversibility for protein release.

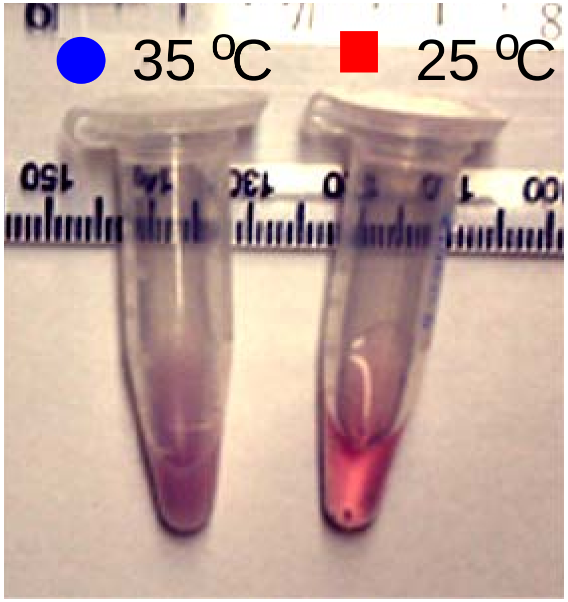
Thermosensitive Gold Nanoparticles

A.D.Q.Li (WSU) and G.J. Exarhos, L-Q Wang PNNL.



Below a critical temperature, the hydrogel is soluble in water (clear solution).

Above T_c, hydrogen bonding between the hydrogel and water solvent is frustrated and a cloudy solution results.



Polymerize PNIPAM hydrogel and functionalize with sulfide groups that bind gold nano-particles.

Oriented Polymeric Nanowires

INEEL, PNNL, SNL

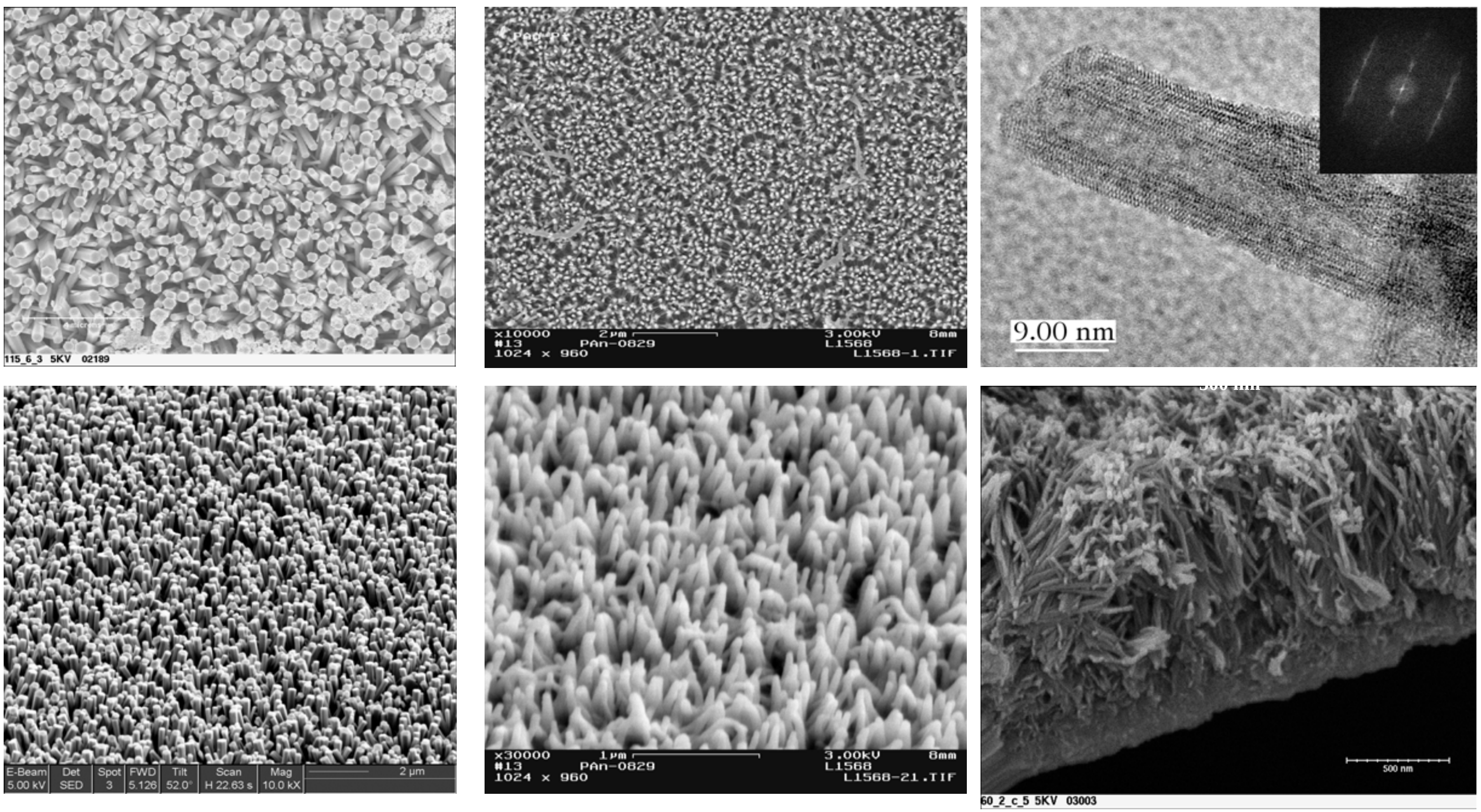
Develop processing approaches to achieve one-dimensional structures with associated ansiotropic properties.

- **Driver** - Physical properties of oriented one-dimensional wires can be exploited for IC, sensor, and catalysis applications.
- **Key research issues**
  - How do solution growth conditions and substrate modification influence growth mechanisms?
  - How are solution deposition conditions modified to promote growth of anisotropic epitaxial films
- **Future directions**
  - Investigate ballistic deposition approaches to forming one-dimensional chiral polymer structures with anisotropic optical, electrical, and magnetic response

Solution-Based Synthesis of One-Dimensional Nanomaterials

J Liu, SNL

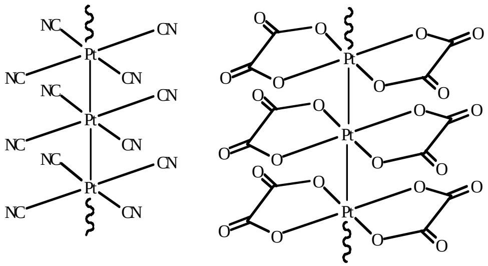
Seeded growth technique using nanoparticle precursors favors epitaxial growth morphology; seeds are deposited using dip coating, electrophoretic deposition, and stamping for micropatterning and subsequent device applications



ZnO | Conducting polymers | TiO2 nanowires/ nanotubes

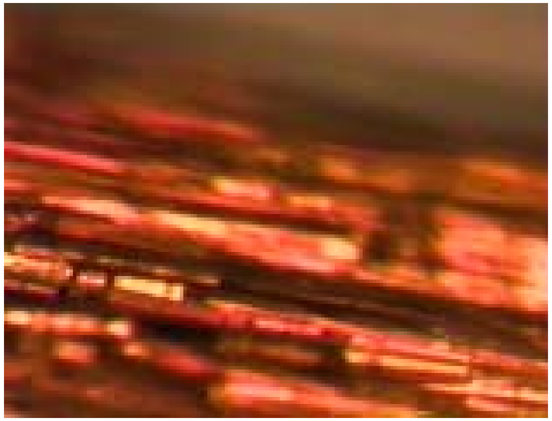
Synthesis/Characterization of Mixed Ligand Platinum-Polymer Nanowires

E. Peterson, INEEL



Stacking of Pt linear polymers in cyano and oxalato complexes.

Potassium cyanoplatinate complex polymerized in bundles



Close-up of K- PtCN polymer bundles protruding from a section of AnoTek 0.02 micron pore diameter filter. Red arrow points to recombination (x2841 Mag.)

Guan-PtOx TEM image showing single nanometer sized wires.

<u>Selected Publications</u>

- L-Q Wang and G.J. Exarhos, *Study of molecular ordering in layered surfactant-silicate mesophase composites*, J. Phys. Chem B. 107:443 (2003).
- M-Q Zhu, L-Q Wang, G.J. Exarhos, and A.D.Q. Li, *Thermosensitive Gold nanoparticles,* JACS 1126(9):2656 (2004).
- I.L. Moudrakovski, L-Q Wang, J.H. Sacher, T. Baumann, G.J. Exarhos, C.I. Raatcliffe, and J.A. Ripmeester, *Probing the geometry and interconnectivity of pores in organic aerogels using hyperpolarized ^{129}Xe NMR spectroscopy*, JACS, In Press (2004).
- A.D.Q.Li, W. Wang, and L-Q Wang, *Folding versus self-assembling*, European J. Chem: A European J. 9(19):4594 (2003).
- J. Liu, Y. Lin, L. Liang, J.A. Voigt, D.L. Huber, Z.R. Tian, E. Coker, B. McKenzie, and M.J. Mcdermott, *Templateless assembly of molecularly aligned conductive polymer nanowires: A new approach for oriented nanostructures*, Chem: A European J. 9:604 (2003).
- Z.R. Tian, J.A. Voigt, J. Liu, B. McKenzie, and H.F. Xu, *Large oriented arrays and continuous films of TiO_2 based nanotubes*, JACS 125:12384 (2003).
- J. Liu, Z.R. Tian, J.A. Voigt, M.J. Macdermot, and B, Mckenzie, *Generalized solution synthesis of large arrays of extended and oriented nanowires*, in <u>Nanowires and Nanobelts</u>, ed. Z.L. Wang, Kluwer Academic Publishers, Norwell, MA p. 239-252 (2003).
- Z.R. Tian, J.A. Voigt, J. Liu, B. Mckenzie, M.J. Mcdermot, R.T. Cygan, and L.J. Criscenti, *Complex ZnO nanostructures*, Nature Materials 2:821 (2003).
- H.B. Eitourni and N.P. Balsara, *Effect of chemical oxidation on the self-assembly of organometallic block copolymers*, JACS, In Press (2004).
- B.C. Anderson, S.M. Cox, P.D. Bloom, V.V. Sheares, and S.K. Mallapragada, *Synthesis and characterization of diblock and gel-forming pentablock copolymers of tertiary amine methacrylates, poly(ethylene glycol) and poly(propylene glycol)*, Macromolecules 36:1670 (2003).
- M.D. Determan, B. Anderson, and S.K. Mallapragada, *Self-assembly of polymers in solution at multiple length scales*, Nature Materials (Submitted) 2004.

Selected Publications, cont.

- S. Jeon and P. V. Braun: Hydrothermal synthesis of Er-doped luminescent TiO_2 nanoparticles, *Chemistry of Materials* 15, 1256-1263 (2003).
- Y.-J. Lee and P. V. Braun: Tunable inverse opal hydrogel pH sensors, *Advanced Materials*, 15, 563-566(2003).
- H. Liang, T. E. Angelini, J.Ho, P. V. Braun and G. C. L. Wong: Molecular imprinting of biomineralized CdS nanostructures: Crystallographic control using self-assembled DNA-membrane templates, *Journal of the American Chemical Society,* 125, 11786-11787 (2003).
- M. A. Meitl, T. M. Dellinger, and P. V. Braun: Bismuth-ceramic nanocomposites with unusual thermal stability via high-energy ball milling, *Advanced Functional Materials,* 13, 795-799 (2003).
- Y.-J Lee, S. A. Pruzinsky and P. V. Braun: Glucose-sensitive inverse opal hydrogels: analysis of optical diffraction response, *Langmuir*, 20, 3096-3106 (2004).
- P. V. Braun: Spontaneous ligand organization, *Nature Materials*, 3, 281-282.
- T.M. Dellinger and P.V. Braun: Lyotropic liquid crystals as nanoreactors for nanoparticle synthesis, *Chemistry of Materials*, ASAP, 2004
- W. Lee, A. Chan, M. A. Bevan, J. A. Lewis and P. V. Braun: Nanoparticle-mediated epitaxial assembly of colloidal crystals on patterned substrates, *Langmuir*, ASAP, 2004
- R. G. Shimmin, A. B. Schoch and P. V. Braun: Polymer size and concentration effects on the size of gold nanoparticles capped by polymeric thiols, *Langmuir*, ASAP, 2004
- Z. S. Zhang, O. M. Wilson, M. Yu. Efremov, W. Senaratne, E. A. Olson, M. Zhang, P. V. Braun, C. K. Ober and L. H. Allen: Heat capacity measurements of two-dimensional self-assembled monolayers on polycrystalline gold, *Applied Physics Letters*, In Press.
- “Solution Equilibria Leading to Formation of Metal-Metal Bonds in Partially Oxidized bis-Oxolato Platinum (II) Systems,” Inorganica Chemica Acta 357 (2004) 833.
- “Synthesis and Characterization of Partially Oxidized Platinum Nanowires, Submitted to Inorganic Chemistry,” April, 2004.
- “Platinum Based Polymeric Materials – INRA Collaborative”, Final Report to INEEL’s LDRD Program, 9/22/03.
- Bernard Anderson, “A study of polymeric platinum(II) compounds and nanoscale materials” Doctoral Dissertation, Montana Stat University, March, 2004.

Program Leveraging with Other DOE Offices

- EM funding – molecular composites for subsurface barriers
- EE funds for high energy power source needs
- "Biorefinery for Production of Polymers and Fuel" DOE, Office of Biomass, EERE; joint project with Metabolix, Inc., FY02-06, ORNL funds - $300K over 3 years
  - Produce biopolymers from green plants
  - polyesters – polyhydroxyalkanoates (PHAs) – have materials properties similar to polyolefins
- DOE EERE
  - Significance – environmentally friendly plastics
  - Renewable, energy eficient, biodegradable, biocompatible
  - Characterize polyesters, blends and copolymers
  - thermodynamics, structure, miscibility, crystallization behavior, processing
  - Smart hydration membranes for PEM fuel cells
- EE/OIT and EM - design for a photonic crystal sensor can be easily integrated into industrial processes and for the detection of industrial wastes, enabling for example; applicability for rapid detection of contaminates at DOE facilities and clean-up operations.

Program Leveraging with Other Agencies, Industry

- Discussions have been held with Wavelength Electronics, Inc., OPTEC of Montana State University and their industrial partners. A joint proposal for submission to Department of Homeland Defense regarding the synthesis and optical property characterization of the materials is in progress.
- Metabolix, Inc, Ecobalance, Inc, Porcelli Consultants, U Tenn, U Central Fl, Cornell, U Akron, U Mass, U Texas
- Significance – environmentally friendly plastics
  - Renewable, energy efficient, biodegradable, biocompatible
  - Characterize polyesters, blends and copolymers, structure, thermodynamics, miscibility, crystallization behavior, processing
- 3M has continued to fund activities through a non-tenured faculty award, and have interviewed a student with the goal of starting a new initiative on three-dimensional polymeric structures for optical applications.
- WPAFB - Holographic patterning of nanoparticle filled polymers.

Notes